

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 June 2002 (13.06.2002)

PCT

(10) International Publication Number  
**WO 02/45530 A2**

(51) International Patent Classification<sup>7</sup>: **A23P 1/00**

(21) International Application Number: PCT/US01/47528

(22) International Filing Date: 5 December 2001 (05.12.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/731,107 6 December 2000 (06.12.2000) US  
10/004,628 4 December 2001 (04.12.2001) US

(71) Applicant (for all designated States except US): **JOHN-SONDIVERSEY, INC.** [US/US]; 8310 16th Street, M/S 509, P.O. Box 902, Sturtevant, Wisconsin 53177-0902 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **MIZUKI, Peter, Y.** [US/US]; 2734 Newman Road, Racine, WI 53406 (US).

(74) Agent: **HAMILTON, Neil, E.**; S. C. Johnson Commercial Markets, Inc., Patent Section, 8310 16th Street - M/S 510, Sturtevant, WI 53177-0902 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOSITION FOR CLEANING FRUITS, VEGETABLES AND FOOD CONTACT SURFACES

(57) Abstract: A composition for cleaning fruits, vegetables and hard, food contact surfaces. The composition contains an edible organic acid, an anionic surfactant, a nonionic surfactant having a hydrophilic-lipophilic balance in the range of between 12 to 16. In one embodiment, the nonionic surfactant is a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative. In a preferred embodiment, the composition is stabilized with a food grade alcohol.

WO 02/45530 A2

## COMPOSITION FOR CLEANING FRUITS, VEGETABLES AND FOOD CONTACT SURFACES

CROSS REFERENCE TO RELATED APPLICATIONS: This is a Continuation-In-Part of patent application Serial No. 09/731,107 filed December 6, 2000.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT: NONE

### BACKGROUND OF THE INVENTION

#### TECHNICAL FIELD

This invention relates to a composition for cleaning fruits, vegetables and hard, food contact surfaces. More particularly, this invention relates to a composition of the foregoing type which is effective in hard water, effective against a broad spectrum of bacteria and effective in wax removal from fruits.

#### BACKGROUND ART

There are available several compositions for cleaning fruits and vegetables. For example, U.S. Patent 4,140,694 discloses a composition for cleaning the surface of food including those of plant origin with a mixture including citric acid, lauryl sulfate and Tween 80 surfactant. In U.S. Patent 5,320,772, there is disclosed a fruit and vegetable cleaning composition which includes sodium lauryl sulfate and nonionic surfactants, such as Tween surfactants. Polyoxyethylene sorbitan fatty acid monoesters are described in U.S. Patent 4,002,579 for cleaning Chinese cabbages. U.S. Patent 5,549,758 teaches the use of clear solutions for cleaning produce with a nonionic surfactant having a hydrophilic-lipophilic balance (HLB) greater than 10. Concerning acid compositions, low HLB are taught.

In order to preserve some fruits and vegetables, they are coated with an oily or waxy coating. In many instances, it is desirable to remove this coating material before ingestion. The prior art does not provide a cleaning composition for fruits and vegetables which is active in hard water, is effective against a broad spectrum of bacteria and can also remove wax.

The objects of the invention therefore are:

- a. Providing an improved composition for cleaning fruits, vegetables and hard, food contact surfaces.

- b. Providing a cleaning composition of the foregoing type which is effective in hard water.
- c. Providing a cleaning composition of the foregoing type which is effective against a broad spectrum of bacteria.
- d. Providing a cleaning composition of the foregoing type which can remove wax from fruit in an efficient manner.

These and still other objects and advantages of the invention will be apparent from the description which follows. In the detailed description below preferred embodiments of the invention will be described in reference to the full scope of the invention. Rather, the invention may be employed in other embodiments.

### SUMMARY OF THE INVENTION

The foregoing objects are accomplished and the shortcomings of the prior art are overcome by the edible fruit, vegetable and hard, food contact surface cleaning composition of this invention which includes in one embodiment an edible organic acid, an anionic surfactant, a nonethoxylated sorbitan derivative, an ethoxylated sorbitan derivative, and water.

In a preferred embodiment, a food grade alcohol such as ethanol is incorporated as a stabilizing agent.

In another embodiment, the sorbitan derivatives are derived from a C<sub>12</sub> - C<sub>18</sub> aliphatic acid.

In yet another embodiment, there is provided an edible fruit, vegetable and hard, food contact surface cleaning composition which includes an edible organic acid, an anionic surfactant, a nonionic surfactant having a HLB in the range of 12 to 16, a food grade alcohol and water.

In a preferred embodiment, the edible organic acid is lactic acid, the anionic surfactant is sodium lauryl sulfate, and the sorbitan derivatives are sorbitan monooleates.

In one aspect, the composition includes about 10%/wt. to about 45%/wt. of an edible organic acid, about 5%/wt. to about 30%/wt. of an anionic surfactant, about 6%/wt. to about 15%/wt. of a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative, and 10%/wt. to about 79%/wt. of water.

In another aspect, the composition includes about 5%/wt. to about 40%/wt. of an edible organic acid, about 5%/wt. to about 15%/wt. of an anionic surfactant, about 6%/wt. to about 15%/wt. of a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative, about 1%/wt. to about 7%/wt. of a food grade alcohol, and 23%/wt. to about 83%/wt. of water.

In a preferred aspect, the composition includes about 16%/wt. of an edible organic acid, about 9.6%/wt. of an anionic surfactant, about 1%/wt. of a nonethoxylated sorbitan derivative, about 12%/wt. of an ethoxylated sorbitan derivative and about 61.4%/wt. water.

In another preferred aspect, the composition includes about 16.9%/wt. of an edible organic acid, about 9.6%/wt. of an anionic surfactant, about 3%/wt. of a nonethoxylated sorbitan derivative, about 12%/wt. of an ethoxylated sorbitan derivative, about 3%/wt. of ethanol and about 56.4%/wt. of water.

In yet another aspect, the nonethoxylated sorbitan derivative and the ethoxylated sorbitan derivative are present in a ratio of about 1:4 to 1:12, respectively.

#### **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The following procedures are employed in preparing the compositions of Examples 1 to 51 depending upon whether a liquid or powder form of sodium lauryl sulfate was used.

In the following Examples, the amounts of materials are expressed in terms of weight %.

##### **PROCEDURE A**

1. CHARGE THE DEIONIZED WATER TO A CLEAN DRY MIXING VESSEL. USE COLD WATER.
2. WHILE SITRRING, SIFT IN THE SODIUM LAURYL SULFATE, AVOIDING THE FORMATION OF CLUMPS. STIR UNTIL TOTALLY DISSOLVED.
3. CONTINUE STIRRING, ADD THE CITRIC ACID, FCC USP, ANHYDROUS. STIR UNTIL TOTALLY DISSOLVED.
4. IN A SEPARATE VESSEL, ADD THE POLYOXYETHYLENE (20) SORBITAN MONOOLEATE, START STIRRING THEN ADD THE SORBITAN MONOOLEATE. STIR TO UNIFORMITY. WHILE STIRRING, ADD THE MIXTURE FROM STEP 4. STIR TO UNIFORMITY.

PROCEDURE B

1. CHARGE THE DEIONIZED WATER TO A CLEAN DRY MIXING VESSEL. USE COLD WATER.
2. WHILE STIRRING, ADD THE 30% LIQUID SODIUM LAURYL. STIR UNTIL TOTALLY DISSOLVED.
3. CONTINUE STIRRING, ADD THE CITRIC ACID, FCC USP, ANHYDROUS. STIR UNTIL TOTALLY DISSOLVED.
4. IN A SEPARATE VESSEL, ADD THE POLYOXYETHYLENE (20) SORBITAN MONOOLEATE. START STIRRING, THEN ADD THE SORBITAN MONOOLEATE. STIR TO UNIFORMITY.
5. WHILE STIRRING, ADD THE MIXTURE FROM STEP 4. STIR TO UNIFORMITY.

One of the acids for use in the composition of this invention is citric acid and the preferred anionic surfactant is sodium lauryl sulfate. The preferred sorbitan ester - ethoxylated sorbitan ester mixture is any combination of sorbitan monooleate and ethoxylated sorbitan monooleate that results in a net HLB between 12.2 to 14.2, most preferably 14.2. This is seen in Examples 1-7. It has been found that an HLB of 14.17 results in a more stable product.

The calculation of a net HLB is well known to those skilled in the art, as set forth in Surfactants and Interfacial Phenomena, Second Edition, John Wiley & Sons (1989), pages 326-329, which teachings are incorporated herein by reference.

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
	Citric Acid	10.00	10.00	10.00	10.00	10.00	10.00	16.0
	Sodium Lauryl Sulfate	15.00	15.00	15.00	15.00	15.00	15.00	9.6
Span 80	Sorbitan Monooleate	3.33	2.50	2.00	1.67	1.25	1.00	1.0
Tween 80	Polyoxyethylene (20) Sorbitan Monooleate	6.67	7.50	8.00	8.33	8.75	9.00	12
	Deionized Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
	Net HLB	11.47	12.33	12.86	13.21	13.66	13.93	14.17
	1:100 dilution, 24 hours*	ppt	clear	clear	clear	clear	clear	clear**
	1:100 dilution, 48 hours*	ppt	clear	clear	clear	clear	clear	clear**

\* 300 ppm hard water

\*\* Indicate a 1:150 dilution for both 24 and 48 hours.

It should be pointed out that sorbitan ester – ethoxylated sorbitan ester combinations, when diluted without the acid – anionic surfactant present, themselves form cloudy solutions.

Optionally, the sorbitan monooleate and the ethoxylated sorbitan monooleate may be substituted in whole or in part with other sorbitan derivatives of monolaurate, monopalmitate, monostearate, trioleate. Preferred are the liquid forms (sorbitan monooleate, sorbitan monolaurate and sorbitan trioleate). The solid forms can be used if liquefied by heating all the ingredients, but limits the dilution phase to while the concentrate is still warm (the concentrate will solidify as it cools to room temperature). The solutions, however, exhibit water-clear stability when diluted in 600 ppm hardness water. Use of other sorbitan derivatives increases the effective net HLB range to between 12.2 and 15.9, again with the most preferable net HLB being 13.3. This is seen in Examples 8-20.



	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20
	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000
	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000	15.0000
Span 20	4.1980	0.0000	3.2860	2.5400	4.1980	--	--	--	--	--	--	--	--
Span 80						2.7420	2.0350	1.5090	1.5890	--	--	--	--
Span 85										2.2820	1.6670	1.2210	1.2650
Tween 20	5.8020	--	--	--	--	7.2580	--	--	--	7.7180	--	--	--
Tween 21	--	10.0000	--	--	--	--	--	--	--	--	--	--	--
Tween 40	--	--	6.7140	--	--	--	7.9650	--	--	--	8.3330	--	--
Tween 60	--	--	--	7.4600	--	--	--	8.4910	--	--	--	7.7790	--
Tween 80	--	--	--	--	5.8020	--	--	--	8.4110	--	--	--	8.7350
Deionized Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
Net HLB Span+Tween	13.30	13.30	13.30	13.30	13.30	13.30	13.30	13.30	13.30	13.30	13.30	13.30	13.30
1:100 dilution, 24 hours*	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear
1:100 dilution, 48 hours*	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear	clear

\*600 ppm hard water

Alternatively, the sorbitan ester – ethoxylated sorbitan ester can be substituted with other toxicologically acceptable nonionic surfactant(s) (e.g., derived from edible oils) if the net HLB is in the range between 12.2 and 15.9, with the most preferable net HLB being 13.3

Optionally, citric acid may be substituted in whole or in part with food grade acids such as benzoic, lactic and acetic acids. This is depicted in the following Example 21.

		<b>Ex. 21</b>
	Lactic Acid	10.56
	Sodium Lauryl Sulfate	15.00
Span 80	Sorbitan Monooleate	2.00
Tween 80	Polyoxyethylene (20) Sorbitan Monooleate	8.00
	Deionized Water	qs to 100
	1:100 dilution, 24 hours*	clear
	1:100 dilution, 48 hours*	clear

\* 300 ppm hard water

From a stability standpoint, it has been found that a 16.9% lactic acid composition is preferred with 9.6% sodium lauryl sulfate and 13% of the sorbitan esters. However, the composition is a 1:150 dilution for 24 hours in 300 ppm hard water.

As shown in Examples 22 and 23, sodium lauryl sulfate may be substituted optionally in whole or in part by other toxicologically acceptable anionic surfactants such as dodecyl benzene sulfonic acid.

		<b>Ex. 22</b>	<b>Ex. 23</b>
	Citric Acid	10.00	15.00
	Sodium Lauryl Sulfate	15.00	--
	Dodecyl Benzene Sulfonic Acid	--	15.00
Span 80	Sorbitan Monooleate	1.67	1.67
Tween 80	Polyoxyethylene (20) Sorbitan Monooleate	8.33	8.33
	Deionized Water	qs to 100	qs to 100
	1:100 dilution, 24 hour*	clear	clear
	1:100 dilution, 48 hour*	clear	clear

\* 300 ppm hard water

For use, and as seen in Examples 1-46, the concentrate is diluted with potable water at the rate of 1:100 concentrate: water. To illustrate the enhanced stability of the invention, the concentrate is diluted with water containing 300 or 600 ppm hardness ions (Ca:Mg ratio 2:1). The water is prepared according to the method in ASTM D 3050-72T. This is shown in Example 24.

#### Ex. 24

##### Hard Water Stock Solution

###### Materials

Calcium Chloride Dihydrate  
Magnesium Chloride Hexahydrate  
1 liter Volumetric Flask  
Balance +/- .0005 Accuracy  
Deionized Water

Prepare a hard water stock solution by dissolving

2.940 +/- 0.002 grams of Calcium chloride dihydrate

and

2.033 +/- 0.002 grams of Magnesium chloride hexahydrate.

In approximately 300 ml of deionized water in the 1 liter volumetric flask.  
Dilute to 1 liter with additional deionized water.

This solution contains 3,000 ppm hardness (expressed as calcium carbonate) with a Calcium:Magnesium molar ratio of 2:1 .

Source: ASTM Designation D 3050-72T

It is noted that the combination without the sorbitan ester – ethoxylated sorbitan ester combination, the diluted solution becomes cloudy and the anionic – hard water precipitate forms. There is also a minimum quantity of the sorbitan ester – ethoxylated sorbitan ester combination required to effectively inhibit the precipitate formation for periods of time greater than 48 hours. As seen in Examples 25-35 for the monooleate combination the minimum is > 6%.

	Ex. 25	Ex. 26	Ex. 27	Ex. 28	Ex. 29	Ex.30
Citric Acid	10.000	10.000	10.000	10.000	10.000	10.000
Sodium Lauryl Sulfate	15.000	15.000	15.000	15.000	15.000	15.000
Sorbitan Monooleate	0.000	0.159	0.318	0.477	0.636	0.795
Polyoxyethylene (20) Sorbitan Monooleate	0.000	0.841	1.682	2.523	3.364	4.205
Deionized Water	75.000	74.000	73.000	72.000	71.000	70.000
1:100 dilution, 24 hours*	ppt	ppt	ppt	ppt	ppt	ppt
1:100 dilution, 48 hours*	--	--	--	--	--	--

\*600 ppm hard water

	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35
Citric Acid	10.000	10.000	10.000	10.000	10.000
Sodium Lauryl Sulfate	15.000	15.000	15.000	15.000	15.000
Sorbitan Monooleate	0.954	1.113	1.272	1.431	1.590
Polyoxyethylene (20) Sorbitan Monooleate	5.046	5.887	6.728	7.569	8.410
Deionized Water	69.000	68.000	67.000	66.000	65.000
1:100 dilution, 24 hours*	clear	clear	clear	clear	clear
1:100 dilution, 48 hours*	clear	clear	clear	clear	clear

\*600 ppm hard water

The quantity of citric acid and sodium lauryl sulfate is limited by its capability to dissolve to form flowable solutions. Otherwise a gel or paste state is formed which limits the ability to be easily dissolved. The level of citric acid can range up to 45% of the formula concentrate. The level of sodium lauryl sulfate can range up to 30% of the formula concentrate. This is illustrated in the following Examples 36-50.

		Ex. 36	Ex. 37	Ex. 38	Ex. 39	Ex. 40	Ex. 41	Ex. 42	Ex. 43
	Citric Acid	10.00	15.00	20.00	25.00	30.00	35.00	40.00	45.00
	Sodium Lauryl Sulfate	15.00	15.00	15.00	15.00	15.00	15.00	15.00	13.50
Span 80	Sorbitan Monooleate	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Tween 80	Polyoxyethylene (20) Sorbitan Monooleate	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
	Deionized Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
	1:100 dilution, 24 hours*	clear	clear	clear	clear	clear	clear	clear	clear
	1:100 dilution, 48 hours*	clear	clear	clear	clear	clear	clear	clear	clear

\* 300 ppm hard water

		Ex. 44	Ex. 45	Ex. 46	Ex. 47
	Citric Acid	10.00	10.00	10.00	10.00
	Sodium Lauryl Sulfate	15.00	18.00	21.00	24.00
Span 80	Sorbitan Monooleate	1.67	1.67	1.67	1.67
Tween 80	Polyoxyethylene (20) Sorbitan Monooleate	8.33	8.33	8.33	8.33
	Deionized Water	qs to 100	qs to 100	qs to 100	qs to 100
	1:100 dilution, 24 hours*	clear	clear	clear	clear
	1:100 dilution, 48 hours*	clear	clear	clear	clear

\* 300 ppm hard water

	Ex. 48	Ex. 49	Ex. 50
Citric Acid	20.000	15.000	10.000
Sodium Lauryl Sulfate	30.000	22.500	15.000
Sorbitan Monooleate	2.226	1.670	1.113
Polyoxyethylene (20) Sorbitan Monooleate	11.774	8.830	5.887
Deionized Water	36.000	52.000	68.000
form	gel	viscous liquid	liquid

The capacity to vary the level of ingredients in this invention allows various dilution ratios to be used and thus yield different levels of physical characteristics. For example, reducing the level of sodium lauryl sulfate with a corresponding reduction in the sorbitan ester – ethoxylated sorbitan ester mixture still produces a stable concentrate. The dilution has still good wetting properties and is efficacious against gram negative and gram positive bacteria but is less foamy. Less foam is desirable in applications where the article to be cleaned needs to be rinsed with potable water. Alternatively, the level of citric acid can be increased in the concentrate. This allows for use of a higher dilution ratio to produce a less foamy solution that still has good wetting properties and is efficacious against gram negative and gram positive bacteria. This is depicted in the following Examples 51 and 52.

		Ex. 51		Ex. 52	
	Citric Acid	10.00		25.00	
	Sodium Lauryl Sulfate	15.00		15.00	
Span 80	Sorbitan Monooleate	2.00		2.00	
Tween 80	Polyoxyethylene (20) Sorbitan Monooleate	8.00		8.00	
	Deionized Water	qs to 100		qs to 100	
	1:100 dilution*	Staph aureus	+ 0/ 10	--	--
		Salmonella	+ 0/ 10	--	--
		E. coli	+ 0/ 10	--	--
	1:200 dilution*	--	--	Staph aureus	+ 0/ 10
		--	--	Salmonella	+ 0/ 10
		--	--	E. Coli	+ 0/ 10

\*Deionized Water

It has been found that the sorbitan esters have limited stability in the presence of organic acids of the previous compositions. It has been found that addition of small quantities of an alcohol, preferably ethanol, greatly enhances the stability of the sorbitan esters in the compositions. Of the alcohols, ethanol is preferred because it is an edible ingredient.

The preferred acid for the stabilized composition of this invention is lactic acid (FCC grade), and the preferred anionic surfactant is sodium lauryl sulfate (USP grade). The preferred sorbitan derivative is a kosher sorbitan monooleate and the preferred ethoxylated sorbitan derivative is a kosher ethoxylated (20 mole EO) sorbitan monooleate. The kosher sorbitan derivatives are preferred for the source of the aliphatic acid. The preferred alcohol is ethanol, USP grade.

The following procedure is employed in preparing the stabilized compositions:

#### PROCEDURE C

1. Charge the deionized water to a clean dry mixing vessel.
2. While stirring, add the lactic acid. Stir until homogeneous.
3. In a separate vessel, add the polyoxyethylene (20) sorbitan monooleate, sorbitan monooleate, and ethanol. Stir until homogeneous.
4. While stirring, add the mixture from step 3. Stir until homogeneous.
5. While stirring, add the sodium lauryl sulfate. Stir until homogeneous.

Depending on the compositional level of the ingredients, the composition is initially a clear, homogeneous liquid or a hazy liquid within a few hours after completion. Within 7 days after completion, the hazy composition becomes a transparent homogenous liquid of enhanced stability. This is shown in Examples 53 and 54.

	<b>Ex. 53</b>	<b>Ex. 54</b>
Lactic Acid	16.9	16.9
Sodium Lauryl Sulfate	9.6	9.6
Sorbitan Monooleate	3.0	3.0
Polyoxyethylene (20) Sorbitan Monooleate	12.0	12.0
Ethanol	--	3.0
Deionized water	q.s. to 100	q.s. to 100
Appearance after 6 months at room temperature	Phase separated	Clean & homogeneous

As seen in Examples 55-60, the preferred sorbitan ester - ethoxylated sorbitan ester mixture is any combination of sorbitan monooleate and ethoxylated sorbitan monooleate that result in a net HLB between 12.2 and 14.2, most preferably 12.9.

The preferred compositions exhibit water clear stability when diluted in 300 ppm hard water as illustrated by Examples 55-60.

	<b>Ex. 55</b>	<b>Ex. 56</b>	<b>Ex. 57</b>
Lactic Acid	16.9	16.9	16.9
Sodium Lauryl Sulfate	9.6	11.0	12.0
Kosher Sorbitan Monooleate	3.0	3.0	3.0
Kosher Polyoxyethylene (20) Sorbitan Monooleate	12.0	12.0	12.0
Ethanol	3.0	3.0	3.0
Deionized water	q.s. to 100	q.s. to 100	q.s. to 100
Net HLB of Sorbitan mixture	12.9	12.9	12.9
1:170 dilution, 24 hours*	clear	clear	clear
1:170 dilution, 48 hours*	clear	clear	clear

\*300 ppm hard water

	Ex. 58	Ex. 59	Ex. 60
Lactic Acid	8.8	10.0	13.2
Sodium Lauryl Sulfate	9.6	9.6	9.6
Kosher Sorbitan Monooleate	3.0	3.0	3.0
Kosher Polyoxyethylene (20) Sorbitan Monooleate	12.0	12.0	12.0
Ethanol	3.0	3.0	3.0
Deionized water	q.s. to 100	q.s. to 100	q.s. to 100
Net HLB of Sorbitan mixture	12.9	12.9	12.9
1:170 dilution, 24 hours*	clear	clear	clear
1:170 dilution, 48 hours*	clear	clear	clear

\*300 ppm hard water

Alternatively, the sorbitan ester - ethoxylated sorbitan ester can be substituted with other toxicologically acceptable nonionic surfactant(s) (e.g., derived from edible oils) if the net HLB is in the range between 12.2 and 15.9, with the most preferable HLB being 12.9.

Optionally, lactic acid may be substituted in whole or in part with food grade acids such as benzoic and acetic.

Optionally, sodium lauryl sulfate may be substituted in whole or in part with other toxicologically acceptable anionic surfactants such as dodecyl benzene sulfonic acid.

For use, and as seen in Examples 53-60, the concentrate is diluted with potable water at the rate of 1:170 concentrate:water. To illustrate the enhanced stability of the invention, the concentrate is diluted with water containing 300 ppm hardness ions (Ca:Mg ratio 2:1) the water is prepared according to the method on ASTM D 3050-72T. This is shown in previous Example 24.

It is noted that the diluted solutions of compositions without the sorbitan ester-ethoxylated sorbitan ester combinations become cloudy as the anionic - hard water precipitate form. There is also a maximum quantity of the anionic surfactant that the sorbitan ester - ethoxylated sorbitan ester combination can effectively inhibit the formation of the hard water precipitation, as seen in Examples 60-62.



	Ex. 60	Ex. 61	Ex. 62
Lactic Acid	16.9	16.9	16.9
Sodium Lauryl Sulfate	9.6	9.6	15.0
Kosher Sorbitan Monooleate	--	--	3.0
Kosher Polyoxyethylene (20) Sorbitan Monooleate	--	--	12.0
Ethanol	--	3.0	3.0
Deionized water	q.s. to 100	q.s. to 100	q.s. to 100
1:170 dilution, 24 hours*	Precipitate	Precipitate	Precipitate
1:170 dilution, 48 hours*	Precipitate	Precipitate	Precipitate

\*300 ppm hard water

Interestingly, it is also noted that lactic acid, sodium sulfate and deionized water mixtures are not stable, but form solid crystalline precipitates. The sorbitan ester/ethanol mixture stabilizes the compositions against the crystalline precipitation. Ethanol alone also has the effect of stabilizing the composition, but only in higher quantities. Higher quantities are not desirable as the compositions become flammable mixtures. Flammable mixtures pose additional burden as to storage and transportation requirements. This is demonstrated in Examples 63-65.

	Ex. 63	Ex. 64	Ex. 65
Lactic Acid	16.9	16.9	16.9
Sodium Lauryl Sulfate	9.6	9.6	9.6
Kosher Sorbitan Monooleate	--	--	3.0
Kosher Polyoxyethylene (20) Sorbitan Monooleate	--	--	12.0
Ethanol	10.0	20.0	3.0
Deionized water	q.s. to 100	q.s. to 100	q.s. to 100
Composition stability	Precipitate	Stable	Stable
Flash Point (TCC)	>200° F	>200° F	>200° F
1:170 dilution, 24 hours*	Precipitate	Precipitate	Clear
1:170 dilution, 48 hours*	Precipitate	Precipitate	Clear

\*300 ppm hard water

(TCC) is Tag Closed Cup method

The compositions have antimicrobial properties against gram negative and gram positive pathogenic bacteria. When evaluated by the AOAC food contact surface sanitizer test, the preferred composition, diluted with 300 ppm hard water, demonstrated efficacy against *Salmonella choleraesuis* and *Staphylococcus aureus*. This is seen in the following Example 66.

	Ex. 66
Lactic Acid	16.9
Sodium Lauryl Sulfate	9.6
Kosher Sorbitan Monooleate	3.0
Kosher Polyoxyethylene (20 Sorbitan Monooleate	12.0
Ethanol	3.0
Deionized water	q.s. to 100
1:170 dilution* <i>Salmonella choleraesuis</i>	>8 log reduction
1:170 dilution* <i>Staphylococcus aureus</i>	>8 log reduction

\*300 ppm hard water

Examples 67 and 68 demonstrate the efficacy of the invention on produce. The produce samples were inoculated by dipping into dilute suspensions of either *E.coli* O157:H7 or *Listeria monocytogenes*. The inoculated produce was air dried for 24 hours and then exposed to the preferred composition for 5 minutes. The produce was then placed in a sterile bag with 30 mls sterile 0.1% peptone water and massaged or stomached. 1 ml aliquots were serially diluted and surface plated to determine the numbers of *E.coli* or *L.monocytogenes* survivors. D-values (the time it takes to achieve a 1-log reduction) were then determined by linear regression. Values for a 25 ppm chlorine solution are provided for comparison purposes. 25 ppm chlorine solutions are commonly used for washing fruits and vegetables.

	Ex. 67		Ex. 68	
Lactic Acid	16.9			
Sodium Lauryl Sulfate	9.6			
Kosher Sorbitan Monooleate	3.0			
Kosher Polyoxyethylene (20 Sorbitan Monooleate	12.0			
Ethanol	3.0			
Deionized water	q.s. to 100			
Chlorine			25 ppm	
	D-values (seconds)		D-values (seconds)	
<u>Produce</u>	<u>E.coli</u> <u>O157:H7</u>	<u>L.mono-</u> <u>cytogenes</u>	<u>E.coli</u> <u>O157:H7</u>	<u>L.mono-</u> <u>cytogenes</u>
Whole apples	40	42	35	34
Sliced apples	72	78	60	64
Whole lettuce	41	39	37	41
Shredded lettuce	79	82	64	61
Strawberries	39	37	33	37

While ethanol is the preferred alcohol for stabilizing the composition of this invention, other alcohols could be employed such as food grade alcohols.

The compositions of this invention can be employed to wash the following fruits and vegetables:

**Citrus Fruits**

Oranges	Tangelos
Grapefruit	Tangerines
Lemons	Temples
Limes	

**Non-Citrus Fruits**

Apples	Figs	Peaches
Apricots	Grapes	Pears
Avocados	Guavas	Pineapples
Bananas	Honeydews	Plums
Cantaloupes	Kiwifruit	Prunes
Cherries	Nectarines	Strawberries
Cranberries	Olives	Watermelons
Dates	Papayas	

**Vegetables**

Artichokes	Carrots	Lettuce
Asparagus	Cauliflower	Head
Beans, Lima	Celery	Leaf
Beans, Snap	Corn	Romaine
Beets	Cucumbers	Onions
Broccoli	Eggplant	Peas
Brussel Sprouts	Escarole Endive	Peppers
Cabbage	Garlic	Spinach
		Tomatoes

While certain examples have been set forth for the purpose of illustrating the compositions of this invention, other variations and modifications of this invention will be obvious to those skilled in this art. For example, flavors and/or fragrances can be added thereto. This invention is not to be limited except as set forth in the following claims.

CLAIMS

1. A composition for cleaning edible fruits, vegetables, and hard food contact surfaces comprising:

about 10%/wt. to about 45%/wt. of an edible organic acid selected from the group consisting of lactic acid, benzoic acid and acetic acid;

about 5%/wt. to about 30%/wt. of an anionic surfactant;

about 6%/wt. to about 15%/wt. of a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative;

and 10%/wt. to about 79%/wt. of water.

2. The composition of claim 1 wherein the sorbitan derivatives are derived from a C<sub>12</sub> - C<sub>18</sub> aliphatic acid.

3. The composition of claim 2 wherein the aliphatic acid is oleic acid.

4. The composition of claim 2 wherein the aliphatic acid is palmitic acid.

5. The composition of claim 2 wherein the aliphatic acid is stearic acid.

6. The composition of claim 2 wherein the aliphatic acid is lauric acid.

7. The composition of claim 2 wherein the nonethoxylated sorbitan derivative and the ethoxylated sorbitan derivative are present in a ratio of about 1:4 to 1:12, respectively.

8. The composition of claim 1 wherein the anionic surfactant is sodium lauryl sulfate.

9. The composition of claim 1 wherein the sorbitan derivatives are sorbitan monooleates.

10. A composition for cleaning edible fruits, vegetables and hard, food contact surfaces comprising:
  - about 16%/wt. of an edible organic acid selected from the group, the group consisting of lactic acid, benzoic acid and acetic acid;
  - about 9.6%/wt. of an anionic surfactant;
  - about 1%/wt. of a nonethoxylated sorbitan derivative;
  - about 12%/wt. of an ethoxylated sorbitan derivative; and
  - about 61.4%/wt. water.
11. The composition of claim 10 wherein the edible organic acid is citric acid.
12. The composition of claim 10 wherein the anionic surfactant is sodium lauryl sulfate.
13. A composition for cleaning edible fruits, vegetables and hard, food contact surfaces comprising:
  - an edible organic acid;
  - an anionic surfactant;
  - a nonethoxylated sorbitan derivative;
  - an ethoxylated sorbitan derivative;
  - a food grade alcohol; and
  - water
14. The composition of claim 13 wherein the food grade alcohol is ethanol.
15. The composition of claim 14 wherein the edible organic acid is lactic acid.
16. The composition of 14 wherein the non-ethoxylated sorbitan derivative is sorbitan monooleate and the ethanoxylated sorbitan derivative is polyoxyethylene sorbitan.

17. A composition for cleaning edible fruits, vegetables and hard, food contact surfaces comprising:

an edible organic acid;

an anionic surfactant;

a nonionic surfactant having a hydrophilic-lipophilic balance in the range of between 12 to 14;

a food grade alcohol; and

water

18. The composition of claim 17 wherein the food grade alcohol is ethanol.

19. The composition of claim 18 wherein the organic acid is lactic acid.

20. The composition of claim 18 wherein the nonethoxylated sorbitan derivative is sorbitan monooleate and the ethoxylated sorbitan derivative is polyoxyethylene sorbitan.

21. A composition for cleaning edible fruits, vegetables, and hard food contact surfaces comprising:

about 5%/wt. to about 40%/wt. of an edible organic acid selected from the group consisting of lactic acid, benzoic acid and acetic acid;

about 5%/wt. to about 15%/wt. of an anionic surfactant;

about 6%/wt. to about 15%/wt. of a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative;

about 1%/wt. to about 7%/wt. of a food grade alcohol; and

about 23%/wt. to about 83%/wt. of water.

22. A composition for cleaning edible fruits, vegetables, and hard food contact surfaces comprising:

about 16%/wt. of an edible organic acid selected from the group consisting of lactic acid, benzoic acid and acetic acid;

about 9.6%/wt. of an anionic surfactant;

about 3%/wt. of a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative;

about 3%/wt. of ethanol; and

about 56.4%/wt. of water.

23. A method of cleaning edible fruits, vegetables and hard, food contact surfaces comprising contacting the fruits, vegetables and surfaces with the composition of claim 13.

24. A method of cleaning edible fruits, vegetables and hard, food contact surfaces comprising contacting the fruits, vegetables and surfaces with the composition of claim 17.

**THIS PAGE BLANK (USPTO)**



(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 June 2002 (13.06.2002)

PCT

(10) International Publication Number  
**WO 02/045530 A3**

(51) International Patent Classification<sup>7</sup>: **C11D 1/83, 3/20, A23B 7/154, A23P 1/00 // C11D 1:66, 1:14**

(21) International Application Number: **PCT/US01/47528**

(22) International Filing Date: **5 December 2001 (05.12.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
09/731,107 6 December 2000 (06.12.2000) US  
10/004,628 4 December 2001 (04.12.2001) US

(71) Applicant (for all designated States except US): **JOHNSON-DIVERSEY, INC. [US/US]; 8310 16th Street, M/S 509, P.O. Box 902, Sturtevant, Wisconsin 53177-0902 (US).**

(72) Inventor: and

(75) Inventor/Applicant (for US only): **MIZUKI, Peter, Y. [US/US]; 2734 Newman Road, Racine, WI 53406 (US).**

(74) Agent: **HAMILTON, Neil, E.; JohnsonDiversey, Inc., Patent Section, 8310 16th Street - M/S 510, Sturtevant, WI 53177-0902 (US).**

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:  
20 February 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **COMPOSITION FOR CLEANING FRUITS, VEGETABLES AND FOOD CONTACT SURFACES**

(57) Abstract: A composition for cleaning fruits, vegetables and hard, food contact surfaces. The composition contains an edible organic acid, an anionic surfactant, a nonionic surfactant having a hydrophilic-lipophilic balance in the range of between 12 to 16. In one embodiment, the nonionic surfactant is a nonethoxylated sorbitan derivative and an ethoxylated sorbitan derivative. In a preferred embodiment, the composition is stabilized with a food grade alcohol.

WO 02/045530 A3

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/47528

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D1/83 C11D3/20 A23B7/154 A23P1/00 //C11D1:66,  
C11D1:14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D A23B A23P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 512 328 A (MILES INC) 11 November 1992 (1992-11-11) page 2, line 17-27 examples I-III	17, 18, 24
Y	US 4 140 649 A (BOSSERT EDUARD ET AL) 20 February 1979 (1979-02-20) cited in the application column 2, line 30 -column 3, line 45 claims 1, 21-26; examples 1, 5	1-6, 8-13, 15, 16, 21-23
Y	WO 98 33400 A (FRUIT WASH OY) 6 August 1998 (1998-08-06)  page 2, last paragraph -page 3, paragraph 2 examples 1-6; table 1	1-6, 8-13, 15, 16, 21-23

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

30 July 2002

Date of mailing of the international search report

06/08/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Bertran Nadal, J

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/47528

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0512328	A	11-11-1992	CA 2062075 A1	07-11-1992
			EP 0512328 A1	11-11-1992
			JP 5140589 A	08-06-1993
			MX 9202084 A1	01-11-1992
US 4140649	A	20-02-1979	DE 2709750 A1	07-09-1978
WO 9833400	A	06-08-1998	FI 970382 A	31-07-1998
			AU 5867198 A	25-08-1998
			EP 0897268 A1	24-02-1999
			WO 9833400 A1	06-08-1998

**THIS PAGE BLANK (USPTO)**